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ABSTRACT

This document is an instructional module package prepared in objective form for use by an instructor familiar with analytical procedures for determining ammonia nitrogen concentrations in a water or wastewater sample. Included are objectives, instructor guides, student handouts, and transparency masters. This module considers preliminary distillation procedures and nesslerization, titrimetric and selective ion electrode analytical methods.
(Author/RH)

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AMMONIA

Training Module 5.110.2.77

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Mary Jo Bruett

TO THE EDUCATIONAL RESOURCES INFORMATION CENTER (ERIC) AND USERS OF THE ERIC SYSTEM "

Prepared for the

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September, 1977

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| | |
|---|--|
| <u>Module No.</u> | <u>Module Title</u> Determination of Ammonia Nitrogen |
| <u>Approx. Time</u> 12 hours | <u>TOPICS</u> Introduction Preliminary Distillation Introduction to Nesslerization Determination of Ammonia by Colorimetric Method Determination of Ammonia by Titrimetric Method Introduction to the Selective Ion Ammonia Electrode Determination of Ammonia by Ammonia Electrode Review |
| <u>Objective</u> When the participant completes this module he should be able to determine the amount of ammonia nitrogen in a water or wastewater sample by any one of three methods, nesslerization, titration or ammonia electrode. | |
| <u>Instructional Approach</u> Illustrated lecture - discussion - laboratory | |
| <u>References</u> Standard Methods, 14th Ed. Effluent Monitoring Procedures, Nutrients Methods for Chemical Analysis of Waters and Wastes Sawyer & McCarthy, Chemistry for Sanitary Engineers Orion Research, Instruction Manual Ammonia Electrode | |

Instructional Aids

EPA slide-tape is available from:

Eileen Hopewell
National Training Center
Water Programs Operation
Vine & St. Claire St.
Cincinnati, Ohio 45268

Overheads

Typed overheads are an example of overhead layout and content. For classroom use the overhead should be constructed using colored, 1/4 inch dry transfer letters.

Other overheads may be copied directly.

Handouts

Handouts may be copied directly. Section 6 and Section 9.

Lab supplies and apparatus

Supplies and apparatus should be supplied per handouts so that participants may work in groups of 2 or 3.

| | |
|---|--|
| Module No: | Module Title: Determination of Ammonia Nitrogen Submodule Title: |
| Approx. Time: 1 hour | Topic: Introduction |
| Objectives: When the participant completes this topic he should be able to: <ol style="list-style-type: none"> 1. List three methods of determination of ammonia nitrogen. 2. Differentiate between the three most commonly used units for expression of ammonia nitrogen; mg/l NH_3, mg/l NH_4, and mg/l NH_3 as N. 3. Explain why most samples must be pretreated by distillation before the ammonia determination is made. 4. Identify the range of concentrations applicable to the colorimetric method, titrimetric method, and electrode method. 5. Indicate sampling procedures and sample preservation procedures for the ammonia nitrogen analysis. | |
| Instructional Aids: EPA slide-tape, Determination of Ammonia Nitrogen Handout: Sample preservation and Storage Conversion table, Ammonia units Overhead Transparencies | |
| Instructional Approach: Illustrated lecture - discussion | |
| References: <ol style="list-style-type: none"> 1. Standard Methods, 14th Ed. 2. Effluent Monitoring Procedures, Nutrients 3. Methods for Chemical Analysis of Waters and Wastes 4. Sawyer & McCarthy, Chemistry for Sanitary Engineers | |
| Class Assignments: None | |

| | |
|--|---|
| Module No: | Topic: Introduction |
| Instructor Notes: | Instructor Outline: |
| <p>Overhead</p> <p>Methods for Ammonia Page 7</p> <p>Nitrogen series Page 10</p> <p>Slide Tape</p> <p>Determination of NH_3</p> <p>Handout</p> <p>Conversion Table Page 9</p> <p>Overhead</p> <p>Conversion Table Page 9</p> <p>Overhead</p> <p>Interferences Page 8</p> | <p>1. Methods</p> <p>a. List the three most common methods of ammonia nitrogen determination</p> <p>Nesslerization Titrimetric Ammonia electrode</p> <p>b. Describe the three methods as to type of determination.</p> <p>Nesslerization - colorimetric Titrimetric - volumetric Electrode - potentiometric</p> <p>c. Indicate that there are other ammonia methods such as the phenate method.</p> <p>2. Units of Expression</p> <p>a. List the three most common units of expression for ammonia.</p> <p>b. Differentiate between the units</p> <p>c. Demonstrate the use of the conversion table.</p> <p>d. Recommend mg/l ammonia nitrogen as the standard unit of expression.</p> <p>3. Pre-treatment</p> <p>a. Discuss interferences to each of the ammonia nitrogen test methods.</p> <p>b. Describe the distillation method of pre-treatment.</p> <p>c. Indicate interferences that the distillation methods do not remove.</p> |

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|---|---|
| Module No: | Topic: Introduction |
| Instructor Notes: | Instructor Outline: |
| Overhead Sensitivity of Methods Page 6 | 4. Sensitivity of Method a. Indicate the ranges of ammonia nitrogen found in natural waters and in wastewater. b. List the minimum and maximum concentration of ammonia nitrogen applicable to each method. |
| Handout Sample Preservation and Storage Pages 11 - 14 | 5. Sampling and storage a. Discuss sampling for ammonia nitrogen in natural waters and wastewater plants. b. Describe sample preservation procedures and holding times. |

OVERHEAD

SENSITIVITY OF METHODS

| | |
|-------------------|-------------------|
| I. NESSLERIZATION | 0.05 to 1.0 mg/l |
| II. TITRIMETRIC | 0.5 to 25 mg/l |
| III. ELECTRODE | 0.02 to 1000 mg/l |
| KITS | 0.4 to 2.5 mg/l |

OVERHEAD

METHODS FOR AMMONIA NITROGEN

- | | |
|------------------------|---|
| I. NESSLERIZATION | COLORIMETRIC METHOD USED WITH OR WITHOUT A DISTILLATION STEP |
| II. TITRIMETRIC | TITRATION AFTER DISTILLATION |
| III. AMMONIA ELECTRODE | POTENTIOMETRIC METRIC METHOD USED WITH OR WITHOUT A DISTILLATION STEP |

KIT METHODS ARE NORMALLY MODIFICATIONS
OF THE NESSLERIZATION METHOD

OVERHEAD

INTERFERENCES

AROMATIC AMINES

ALIPHATIC AMENES

TURBIDITY

RESIDUAL CHLORINE

CYANATE

MERCURY SALTS

WETTING AGENTS

~~VOLATILE~~ ALKALINES

~~VOLATILE~~ AMINES.

11

CONVERSION FACTORS

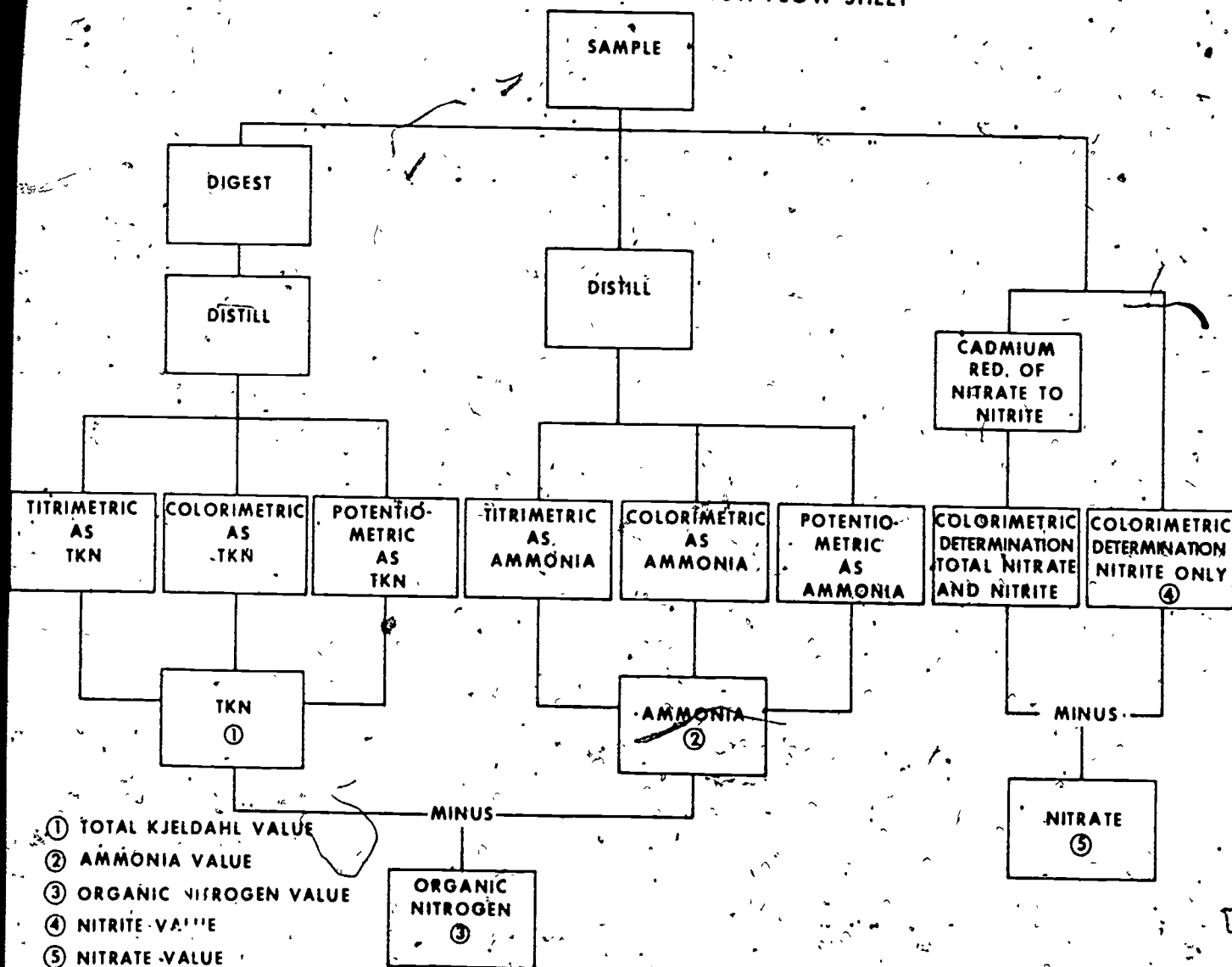
| <u>Multiply</u> | <u>By</u> | <u>To Get</u> |
|-------------------------|-----------|-------------------------|
| mg/l NH_3 as N | 1.22 | mg/l NH_3 |
| mg/l NH_3 as N | 1.29 | mg/l NH_4^+ |
| mg/l NH_3 | .775 | mg/l NH_3 as N |
| mg/l NH_3 | 1.06 | mg/l NH_4^+ |
| mg/l NH_4^+ | .900 | mg/l NH_3 as N |

NH_3 as N = Ammonia as Nitrogen

NH_3 = Ammonia

NH_4 = Ammonium

NITROGEN SERIES DETERMINATION FLOW SHEET



SAMPLE PRESERVATION

Complete and unequivocal preservation of samples, either domestic sewage, industrial wastes, or natural waters, is a practical impossibility. Regardless of the nature of the sample, complete stability for every constituent can never be achieved. At best, preservation techniques can only retard the chemical and biological changes that inevitably continue after the sample is removed from the parent source. The changes that take place in a sample are either chemical or biological. In the former case, certain changes occur in the chemical structure of the constituents that are a function of physical conditions. Metal cations may precipitate as hydroxides or form complexes with other constituents; cations or anions may change valence states under certain reducing or oxidizing conditions; other constituents may dissolve or volatilize with the passage of time. Metal cations may also adsorb onto surfaces (glass, plastic, quartz, etc.), such as, iron and lead. Biological changes taking place in a sample may change the valence of an element or a radical to a different valence. Soluble constituents may be converted to organically bound materials in cell structures, or cell lysis may result in release of cellular material into solution. The well known nitrogen and phosphorus cycles are examples of biological influence on sample composition.

Methods of preservation are relatively limited and are intended generally to (1) retard biological action, (2) retard hydrolysis of chemical compounds and complexes and (3) reduce volatility of constituents.

Preservation methods are generally limited to pH control, chemical addition, refrigeration, and freezing. Table 1 shows the various preservatives that may be used to retard changes in samples.

Many water and waste samples are unstable. In situations where the interval between sample collection and analysis is long enough to produce changes in either the concentration or the physical state of the constituent to be measured, the preservation practices in Table II are recommended.

TABLE I

| <u>Preservative</u> | <u>Action</u> | <u>Applicable to:</u> |
|--|--|--|
| HgCl ₂ | Bacterial Inhibitor | Nitrogen forms, Phosphorous forms |
| Acid (HNO ₃) | Metals solvent, prevents precipitation | Metals |
| Acid (H ₂ SO ₄) | Bacterial Inhibitor | Organic samples (COD, oil & grease organic carbon) |
| | Salt formation with organic bases | Ammonia; amines |
| Alkali (NaOH) | Salt formation with volatile compounds | Cyanides, organic acids |
| Refrigeration | Bacterial Inhibitor | Acidity-alkalinity, organic materials, BOD, color, odor, organic P, organic N, carbon, etc. Biological organism (coliform, etc.) |

In summary, refrigeration at temperatures near freezing or below is the best preservation technique available, but it is not applicable to all types of samples.

The recommended choice of preservatives for various constituents is given in Table 2. These choices are based on the accompanying references and on information supplied by various Regional Analytical Quality Control Coordinators.

TABLE 2

RECOMMENDATION FOR SAMPLING AND PRESERVATION
OF SAMPLES ACCORDING TO MEASUREMENT (1)

| Measurement | Vol. Req. (ml) | Container (2) | Preservative | Holding Time (6) |
|---------------------------|----------------------|---------------|--|---------------------|
| Acidity | 100 | P, G | Cool, 4° C | 24 Hrs. |
| Alkalinity | 100 | P, G | Cool, 4° C | 24 Hrs. |
| BOD | 1000 | P, G | Cool, 4° C | 6 Hrs. (3) |
| COD | 50 | P, G | H ₂ SO ₄ to pH 2 | 7 Days |
| Dissolved Oxygen Probe | 300 | G only | Det. on site | No Holding |
| Winkler | 300 | G only | Fix on site | No Holding |
| Nitrogen | | | | |
| Ammonia | 400 | P, G | Cool, 4° C H ₂ SO ₄ to pH 2 | 24 Hrs. |
| Kjeldahl | 500 | P, G | Cool, 4° C H ₂ SO ₄ to pH 2 | 24 Hrs. (4) |
| Nitrate | 100 | P, G | Cool, 4° C H ₂ SO ₄ to pH 2 | 24 Hrs. (4) |
| Nitrite | 50 | P, G | Cool, 4° C | 24 Hrs. (4) |
| Oil & Grease | 1000 | G only | Cool, 4° C H ₂ SO ₄ to pH 2 | 24 Hrs. |
| pH | 25 | P, G | Cool, 4° C Det. on site | 6 Hrs. |
| Residue | | | | |
| Filterable | 100 | P, G | Cool, 4° C | 7 Days |
| Non-Filterable | 100 | P, G | Cool, 4° C | 7 Days |
| Total | 100 | P, G | Cool, 4° C | 7 Days |
| Volatile | 100 | P, G | Cool, 4° C | 7 Days |

TABLE 2 Cont.)

| Measurement | Vol. Req. (ml) | Container (2) | Preservative | Holding Time (6) |
|----------------------|----------------|---------------|--------------|------------------|
| Settleable Matter | 1000 | P, G | None Req. | 24 Hrs. |
| Specific Conductance | 100 | P, G | Cool, 40° C | 24 Hrs. |
| Temperature | 1000 | P, G | Det. on site | No Holding |
| Turbidity | 100 | P, G | Cool, 40° C | 7 Days |

1. More specific instructions for preservation and sampling are found with each procedure as detailed in this manual. A general discussion on sampling water and industrial wastewater may be found in ASTM, Part 23, p. 72 - 91 (1973).
2. Plastic or Glass
3. If samples cannot be returned to the laboratory in less than 6 hours and holding time exceeds this limit, the final reported data should indicate the actual holding time.
4. Mercuric chloride may be used as an alternate preservative at a concentration of 40 mg/l, especially if a longer holding time is required. However, the use of mercuric chloride is discouraged whenever possible.
5. If the sample is stabilized by cooling, it should be warmed to 25° C for reading, or temperature correction made and results reported at 25° C.
6. It has been shown that samples properly preserved may be held for extended periods beyond the recommended holding time.

| | |
|---|--|
| Module No: | Module Title: Determination of Ammonia Nitrogen |
| Approx. Time: 2 hours | Submodule Title: Topic: Preliminary Distillation |
| Objectives: When the participant completes this topic he should be able to: <ol style="list-style-type: none"> 1. Identify the proper apparatus and reagents needed for the preliminary distillation step in the ammonia nitrogen test. 2. Conduct a preliminary distillation of ammonia nitrogen. 3. Properly store a distilled ammonia sample for the ammonia nitrogen test. | |
| Instructional Aids: laboratory apparatus and reagents listed in handout Handout: Ammonia Nitrogen procedures Overheads | |
| Instructional Approach: Laboratory | |
| References: Standard Methods, 14th Ed Methods for Chemical Analysis of Waters and Wastes (EPA) | |
| Class Assignments: Conduct a preliminary ammonia distillation | |

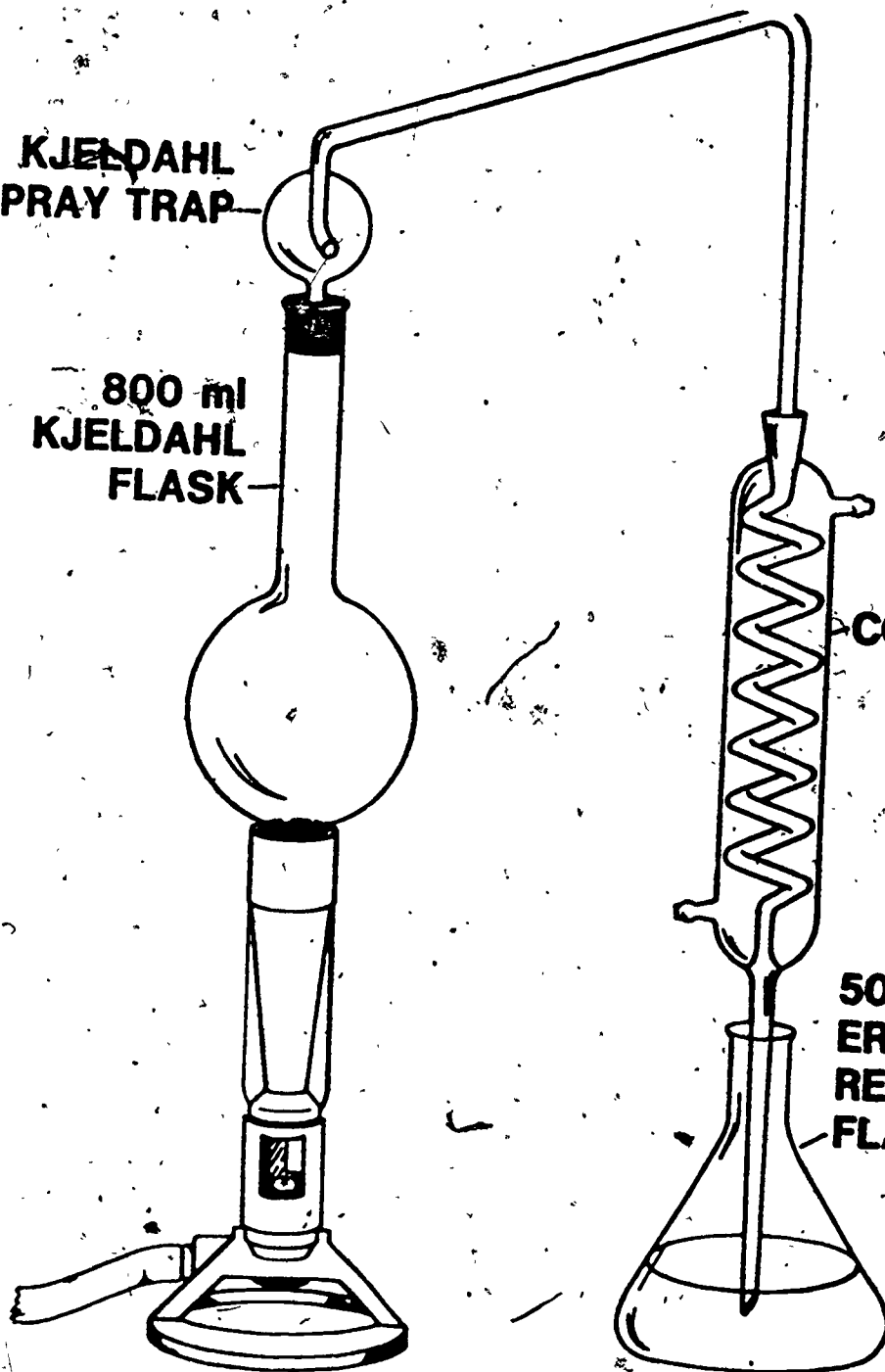
| | |
|---|---|
| Module No: | Topic: Preliminary Distillation |
| Instructor Notes: | Instructor Outline: |
| Handout: Ammonia Nitrogen Procedures - Section 5 and 6 Pages 18 - 27 Overhead Ammonia distillation setup Page 17 Handout Ammonia Procedures Sections 7.1 - 7.3 Pages 18 - 27 | <ol style="list-style-type: none">1. Apparatus and Reagents<ol style="list-style-type: none">a. Show and describe the apparatus needed for distillation of ammonia.b. Demonstrate the makeup of required reagents and indicate the availability of premade reagents.2. Preliminary Distillation<ol style="list-style-type: none">a. Demonstrate the startup and end of an ammonia distillation.b. Have participants conduct a preliminary distillation3. Sample Storage<ol style="list-style-type: none">a. Discuss storage of distilled ammonia samples. |

KJELDAHL
SPRAY TRAP

800 ml
KJELDAHL
FLASK

CONDENSER

500 ml
ERLENMEYER
RECEIVING
FLASK



NITROGEN, AMMONIA

(Distillation Procedure)
Nesslerization Procedure
Titrimetric Indicator Procedure

1. Scope and Application

1.1 This distillation method covers the determination of ammonia-nitrogen exclusive of total Kjeldahl nitrogen, in drinking, surface, and saline waters, domestic and industrial wastes. It is the method of choice where economics and sample load do not warrant the use of automated equipment.

1.2 The method covers the range from about 0.05 to 1.0 mg/l $\text{NH}_3 - \text{N}$ /l for the colorimetric procedures, from 1.0 to 25 mg/l for the titrimetric procedure and from 0.05 to 1400 mg/l for the electrode method.

1.3 This method is described for macro glassware; however, micro distillation equipment may also be used.

2. Summary of Method

2.1 The sample is buffered at a pH of 9.5 with a borate buffer in order to decrease hydrolysis of cyanates and organic nitrogen compounds, and is then distilled into a solution of boric acid. The ammonia in the distillate can be determined colorimetrically by nesslerization, titrimetrically with sulfuric acid with the use of a mixed indicator, or potentiometrically by the ammonia electrode. The choice between the first two procedures depends on the concentration of the ammonia.

3. Sample Handling and Preservation

3.1 Samples may be preserved with 2 ml of conc. H_2SO_4 or 40 mg HgCl_2 per liter and stored at 40° C.

4. Interferences

4.1 A number of aromatic and aliphatic amines, as well as other compounds, both organic and inorganic, will cause turbidity upon the addition of Nessler reagent, so direct nesslerization (i.e. without distillation), has been discarded as an official method.

4.2 Cyanate, which may be encountered in certain industrial effluents, will hydrolyze to some extent even at the pH of 9.5 which distillation is carried out. Volatile alkaline compounds, such as certain ketones, aldehydes, and alcohols, may cause an off-color upon nesslerization in the distillation method. Some of these, such as formaldehyde, may be eliminated by boiling off at a low pH (approximately 2 to 3) prior to distillation and nesslerization.

4.3 Residual chlorine must also be removed by pretreatment of the sample with sodium thiosulfate before distillation.

4.4 If the sample has been preserved with a mercury salt, the mercury ion must be complexed with sodium thiosulfate (0.2 g) prior to distillation.

5. Apparatus

5.1 An all-glass distilling apparatus with an 800 - 1000 ml flask.

5.2 Spectrophotometer or filter photometer for use at 425 nm and providing a light path of 1 cm. or more.

5.3 Nessler tubes: Matched Nessler tubes (APHA Standard) about 300 mm long, 17 mm inside diameter, and marked at 225 mm \pm inside measurement from bottom.

5.4 Erlenmeyer flasks: The distillate is collected in 500 ml glass-stoppered flasks. These flasks should be marked at the 350 and the

500 ml volumes. With such marking, it is not necessary to transfer the distillate to volumetric flasks.

6. Reagents

6.1 Distilled water should be free of ammonia. Such water is best prepared by passage through an ion exchange column containing a strongly acidic cation exchange resin mixed with a strongly basic anion exchange resin. Regeneration of the column should be carried out according to the manufacturer's instructions.

Note: All solutions must be made with ammonia-free water.

6.2 Ammonium chloride, stock solution:

1.0 ml = 1.0 mg $\text{NH}_3 - \text{N}$. Dissolve 3.819 g $\text{NH}_4 \text{Cl}$ in distilled water and bring to volume in a 1 liter volumetric flask.

6.3 Ammonium chloride, standard solution:

1.0 ml = 0.01 mg. Dilute 10.0 ml of stock solution (6.2) to 1 liter in a volumetric flask.

6.4 Boric acid solution (20 g/l): Dissolve 20 g H_3BO_3 in distilled water and dilute to 1 liter.

6.5 Mixed indicator: Mix 2 volumes of 0.2% methyl red in 95% ethyl alcohol with 1 volume of 0.2% methylene blue in 95% ethyl alcohol. This solution should be prepared fresh every 30 days.

Note 2: Specially denatured ethyl alcohol conforming to Formula 3A or 30 of the U. S. Bureau of Internal Revenue may be substituted for 95% ethanol.

6.6 Nessler reagent: Dissolve 100 g of mercuric iodide and 70 g of potassium iodide in a small amount of water. Add this mixture slowly,

with stirring to a cooled solution of 160 g of NaOH in 500 ml of water. Dilute the mixture to 1 liter. If this reagent is stored in a Pyrex bottle out of direct sunlight, it will remain stable for a period of up to 1 year.

Note 3: This reagent should give the characteristic color with ammonia within 10 minutes after addition, and should not produce a precipitate with small amounts of ammonia (0.04 mg in a 50 ml volume).

6.7 Borate buffer: Add 88 ml of 0.1 N NaOH solution to 500 ml of 0.025 M sodium tetraborate solution (5.0 g anhydrous $\text{Na}_2\text{B}_4\text{O}_7$ or 9.5 g $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ per liter) and dilute to 1 liter.

6.8 Sulfuric acid, standard solution: (0.02 N, 1 ml = 0.28 mg NH_3 - N).

Prepare a stock solution of approximately 0.1 N acid by diluting 3 ml of conc. H_2SO_4 (sp. gr. 1.84) to 1 liter with CO_2 free distilled water. Dilute 200 ml of this solution to 1 liter with CO_2 free distilled water.

Note 4: An alternate and perhaps preferable method is to standardize the approximately 0.1 N H_2SO_4 solution against a 0.100 N Na_2CO_3 solution. By proper dilution the 0.02-N acid can then be prepared.

6.8.1 Standardize the approximately 0.02 N acid against 0.0200 N Na_2CO_3 solution. This last solution is prepared by dissolving 1.060 g anhydrous Na_2CO_3 , oven-dried at 140°C , and diluting to 1000 ml with CO_2 free distilled water.

6.9 Sodium hydroxide, 1 N: Dissolve 40 g NaOH in ammonia-free water and dilute to 1 liter.

6.10 Dechlorinating reagents: A number of dechlorinating reagents may be used to remove residual chlorine prior to distillation. These include:

- a. Sodium thiosulfate (1/70 N): Dissolve 3.5 g $\text{Na}_2\text{S}_2\text{O}_3$ in distilled water and dilute to 1 liter. One ml of this solution will remove 1 mg/l of residual chlorine in 500 ml of sample.
- b. Sodium arsenite (1/70 N): Dissolve 1.0 g NaAsO_2 in distilled water and dilute to 1 liter.

7. Procedure

7.1 Preparation of equipment: Add 500 ml of distilled water to an 800 ml Kjeldahl flask. The addition of boiling chips which have been previously treated with dilute NaOH will prevent bumping. Steam out the distillation apparatus until the distillate shows no trace of ammonia with Nessler reagent.

7.2 Sample preparation: Remove the residual chlorine in the sample by adding dechlorinating agent equivalent to the chlorine residual. To 400 ml of sample add 1 N NaOH (6.9), until the pH is 9.5, checking the pH during addition with a pH meter or by use of a short range pH paper.

7.3 Distillation: Transfer the sample, the pH of which has been adjusted to 9.5, to an 800 ml Kjeldahl flask and add 25 ml of the borate buffer (6.7). Distill 300 ml at the rate of 6 - 10 ml/min. into 50 ml of 2% boric acid (6.4) contained in a 500 ml Erlenmeyer flask.

Note 5: The condenser tip or an extension of the condenser tip must extend below the level of the boric acid solution.

Dilute the distillate to 500 ml with distilled water and nesslerize an aliquot to obtain an approximate value of the ammonia-nitrogen concentration. For concentrations above 1 mg/l the ammonia should be determined titrimetrically. For concentrations below this value it is

determined colorimetrically. The electrode method may also be used.

7.4 Determination of ammonia in distillate: Determine the ammonia content of the distillate titrimetrically, colorimetrically or potentiometrically as described below.

7.4.1 Titrimetric Determination: Add 3 drops of the mixed indicator to the distillate and titrate the ammonia with the 0.02 N H_2SO_4 , matching the end point against a blank containing the same volume of distilled water and H_3BO_3 solution.

7.4.2 Colorimetric determination: Prepare a series of Nessler tube standards as follows:

| ml of Standard | |
|-----------------------------|-----------------------|
| 1.0 ml = 0.01 mg $NH_3 - N$ | mg $NH_3 - N/50.0$ ml |
| 0.0 | 0.0 |
| 0.5 | 0.005 |
| 1.0 | 0.01 |
| 2.0 | 0.02 |
| 3.0 | 0.03 |
| 4.0 | 0.04 |
| 5.0 | 0.05 |
| 8.0 | 0.08 |
| 10.0 | 0.10 |

Dilute each tube to 50 ml with distilled water, add 1.0 ml of Nessler reagent (6.6) and mix. After 20 minutes read the optical densities at 425 nm against the blank. From the values obtained plot optical density (absorbance) vs. mg $NH_3 - N$ for the standard curve.

7.4.3 Potentiometric determination: Consult the method entitled Nitrogen Ammonia: Selective Ion Electrode Method in this manual.

7.4.4 It is not imperative that all standards be distilled in the same manner as the samples. It is recommended that at least two standards (a high and low) be distilled and compared to similar values on the curve to insure that the distillation technique is reliable. If distilled standards do not agree with undistilled standards the operator should find the cause of the apparent error before proceeding.

7.5 Determine the ammonia in the distillate by nesslerizing 50 ml or an aliquot diluted to 50 ml and reading the optical density at 425 nm as described above for the standards. Ammonia-nitrogen content is read from the standard curve.

8. Calculations

8.1 Titrimetric

$$\text{mg/l NH}_3 - \text{N} = \frac{A \times 0.28 \times 1000}{S}$$

Where

A = ml 0.02 N H₂SO₄ used

S = ml sample

8.2 Spectrophotometric

$$\text{mg/l NH}_3 - \text{N} = \frac{A \times 1000}{D} \times \frac{B}{C}$$

Where

A = mg NH₃ - N read from standard curve

B = ml total distillate collected, including boric acid and dilution

C = ml distillate taken for nesslerization

D = ml of original sample taken

8.3 Potentiometric

$$\text{mg/l NH}_3 - \text{N} = \frac{500}{D} \times A$$

Where

A = mg NH₃ - N/l from electrode method standard curve

D = ml of original sample taken

9. Precision and Accuracy

9.1 Twenty-four analysts in sixteen laboratories analyzed natural water samples containing exact increments of an ammonium salt, with the following results:

| Increment as Nitrogen, Ammonia- mg/ N/liter | Precision as Standard Deviation mg N/liter | Accuracy as | |
|---|--|-------------|--------------------|
| | | Bias % | Bias mg N/liter |
| 0.21 | 0.122 | -5.54 | -0.01 |
| 0.26 | 0.070 | -18.12 | -0.05 |
| 1.71 | 0.244 | +0.46 | +0.01 |
| 1.92 | 0.279 | -2.01 | -0.04 |

(FWPCA Method Study 2, Nutrient Analyses)

LABORATORY DATA SHEET

Nitrogen, Ammonia Determination
(Sample contains 1.0 to 25.0 mg/l $\text{NH}_3\text{-N}$).

Sample No. _____ Date/Time Sampled _____ Sample Point _____

(Sulfuric acid. 0.02N ml _____) (0.28) (1000)
Sample ml _____ = _____ mg/liter $\text{NH}_3\text{-N}$

Analyst _____ Date _____

LABORATORY DATA SHEET

Nitrogen, Ammonia Determination
(Sample Contains 0.05 to 1.0 mg/liter $\text{NH}_3\text{-N}$)

Sample No. _____ Date/Time Sampled _____ Sample Point _____

$$\frac{(\text{mg of } \text{NH}_3\text{-N}) (1000)}{(\text{Sample ml})} \times \frac{(\text{Total Distillate* Collected ml})}{(\text{Distillate Taken for Nesslerization ml})} = \text{mg/l } \text{NH}_3\text{-N}$$

Analyst _____

Date _____

*Include boric acid plus dilution water

| | |
|--|--|
| Module No.: | Module Title: Determination of Ammonia Nitrogen |
| | Submodule Title: |
| Approx. Time: 30 Min. | Topic: Introduction to Nesslerization |
| Objectives: Upon the completion of this topic the participant should be able to: <ol style="list-style-type: none"> 1. List interferences to the nesslerization method of ammonia nitrogen analysis. 2. Indicate when direct nesslerization method is applicable. 3. Indicate why nesslerization cannot be used on ammonia nitrogen concentrations above one milligram per liter. | |
| Instructional Aids: none | |
| Instructional Approach: Lecture - discussion | |
| References: Standard Methods, 14th Ed. | |
| Class Assignments: None | |

| | |
|-------------------|---|
| Module No: | Topic: Introduction to Nesslerization |
| Instructor Notes: | Instructor Outline: <ol style="list-style-type: none">1. Interferences<ol style="list-style-type: none">a. Discuss interferences to the nesslerization method.b. Indicate how the interferences may be removed.2. Direct Nesslerization<ol style="list-style-type: none">a. Describe direct nesslerization and indicate the type of samples it may be used on.3. Discuss problem encountered when the nesslerization method is used for concentration of greater than 1 mg/l. Discuss problems encountered in diluting samples down to the 1 mg/l range. |

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| Module No: | Module Title: Determination of Ammonia Nitrogen |
| Approx. Time: 30 Min. | Submodule Title: Topic: Determination of Ammonia by Colorimetric Method |
| Objectives: Upon completion of this topic the participant should be able to: <ol style="list-style-type: none"> 1. Identify the proper apparatus and reagents needed for the colorimetric (Nesslerization) method for ammonia nitrogen. 2. Conduct a colorimetric ammonia determination given proper test equipment, reagents, procedures sheet, and predistilled sample. 3. Translate the raw data from the test into proper units of expression given appropriate conversion factors and equations. | |
| Instructional Aids: Apparatus and reagents listed in handouts Handout Ammonia Procedure Ammonia Procedures using kits | |
| Instructional Approach: Lab | |
| References: EPA Methods Manual | |
| Class Assignments: Perform the Ammonia Analysis in class in groups | |

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| Module No: | Topic: Determination of Ammonia by Colorimetric Method |
| Instructor Notes: | Instructor Outline: |
| <p>Handout</p> <p>Ammonia Procedures Sections 5 and 6 Pages 18 - 27</p> <p>Handout</p> <p>Ammonia Procedures with Kits Pages 32 - 35</p> <p>Handout</p> <p>Ammonia Procedures Sections 7.4.2 7.5 8.2 Pages 18 - 27</p> | <ol style="list-style-type: none"> 1. Apparatus and reagents <ol style="list-style-type: none"> a. Show and describe the apparatus needed for nesslerization. b. Demonstrate the makeup of required reagents and indicate the availability of premade reagents. c. Demonstrate the makeup of standards and use of standard curve. d. Discuss the use of ammonia kits. 2. Nesslerization ammonia determination <ol style="list-style-type: none"> a. Demonstrate the nesslerization method and the makeup of a standard curve. b. Have participants conduct a nesslerization ammonia determination. 3. Calculations <ol style="list-style-type: none"> a. Demonstrate the conversion of raw data into standard units. b. Have participants calculate results. |

NITROGEN, AMMONIA

Distillation Kit Procedure

1. Scope and Application

1.1 This distillation method covers the determination of ammonia-nitrogen exclusive of total Kjeldahl nitrogen, in drinking, surface, and saline waters, domestic and industrial wastes using commercial ammonia kits.

1.2 The method covers the range from 1.0 to 25 mg/l.

2. Summary of Method

2.1 The sample is buffered at a pH of 9.5 with a borate buffer in order to decrease hydrolysis of cyanates and organic nitrogen compounds, and is then distilled into a solution of boric acid. The ammonia is the distillate is determined with the use of commercially available kits.

3. Sample Handling and Preservation

3.1 Samples may be preserved with 2 ml of conc. H_2SO_4 or 40 mg $HgCl_2$ per liter and stored at 4° C.

4. Interferences

4.1 Cyanate, which may be encountered in certain industrial effluents, will hydrolyze to some extent even at the pH of 9.5 at which distillation is carried out.

4.2 Residual chlorine must also be removed by pretreatment of the sample with sodium thiosulfate before distillation.

4.3 If the sample has been preserved with a mercury salt, the mercury ion must be complexed with sodium thiosulfate (0.2 g) prior to distillation.

5. Apparatus

5.1 An all-glass distilling apparatus with an 800 - 1000 ml flask.

5.2 Erlenmeyer flasks: The distillate is collected in 500 ml glass stoppered flasks. These flasks should be marked at the 350 and the 500 ml volumes. With such marking, it is not necessary to transfer the distillate to volumetric flasks.

5.3 pH meter and electrodes

6. Reagents

6.1 Distilled water should be free of ammonia. Such water is best prepared by passage through an ion exchange column containing a strongly acidic cation exchange resin mixed with a strongly basic anion exchange resin. Regeneration of the column should be carried out according to the manufacturer's instructions.

Note: All solutions must be made with ammonia-free water.

6.2 Boric acid solution (20 g/l): Dissolve 20 g H_3BO_3 in distilled water and dilute to 1 liter.

6.3 Borate buffer: Add 88 ml of 0.1 N NaOH solution to 500 ml of 0.025 M sodium tetraborate solution (5.0 g anhydrous $Na_2B_4O_7$ or 9.5 g $Na_2B_4O_7 \cdot 10H_2O$ per liter) and dilute to 1 liter.

6.4 Dechlorinating reagents: A number of dechlorinating reagents may be used to remove residual chlorine prior to distillation. These include:

a. Sodium thiosulfate (1/70 N): Dissolve 3.5 g $Na_2S_2O_3$ in distilled water and dilute to 1 liter. One ml of this solution will remove 1 mg/l of residual chlorine in 500 ml of sample.

b. Sodium arsenite (1/70 N): Dissolve 1.0 g $NaAsO_2$ in distilled water and dilute to 1 liter.

7. Procedure

7.1 Preparation of equipment: Add 500 ml of distilled water to an 800 ml Kjeldahl flask. The addition of boiling chips which have been previously treated with dilute NaOH will prevent bumping. Steam out the distillation apparatus until the distillate shows no trace of ammonia with Nessler reagent.

7.2 Sample preparation: Remove the residual chlorine in the sample by adding dechlorinating agent equivalent to the chlorine residual. To 400 ml of sample add 1 N. NaOH (6.9), until the pH is 9.5, checking the pH during addition with a pH meter or by use of a short range pH paper.

7.3 Distillation: Transfer the sample, the pH of which has been adjusted to 9.5 to an 800 ml Kjeldahl flask and add 25 ml of the borate buffer (6.7). Distill 300 ml at the rate of 6 - 10 ml/min. into 50 ml of 2% boric acid (6.4) contained in a 500 ml Erlenmeyer flask.

Note 5: The condenser tip or an extension of the condenser tip must extend below the level of the boric acid solution. Dilute the distillate to 500 ml with distilled water and nesslerize an aliquot to obtain an approximate value of the ammonia-nitrogen concentration.

7.4 Determination of ammonia in distillate by use of commercial kits.

7.4.1 Dilute the distillate to the range of the kit with ion-free water.

7.4.2 Determine the ammonia concentration following directions furnished with the commercial kit.

8. Calculate the ammonia level in the original sample using the following formula:

$$\frac{\text{Distillate volume} \times D}{\text{Sample volume} \times V} \times \text{kit concentration} = \text{mg/l NH}_3 \text{ as N}$$

D = diluted volume (dilution water + sample)

V = volume diluted

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| Module No: | Module Title: Determination of Ammonia Nitrogen |
| Approx. Time: 1 hour | Submodule Title: Topic: Determination of Ammonia by Titrimetric Method |
| Objectives: Upon the completion of this topic the participant should be able to: <ol style="list-style-type: none"> 1. Identify the proper apparatus and reagents needed for the ammonia nitrogen test by the titrimetric method. 2. Conduct a titrimetric ammonia nitrogen determination given proper test equipment, reagents, procedures sheet and pre-distilled sample. 3. Translate the raw data from the test into proper units of expression given appropriate conversion factors and equations. | |
| Instructional Aids: Apparatus and Reagents as listed in Handout (HO-4) Handout Ammonia Procedures, Titrimetric Method (HO-4) Overheads | |
| Instructional Approach: Laboratory | |
| References: Standard Methods 14th Ed Products/Procedures Manual for Water/Wastewater Analysis by Fisher Scientific Co. W/W77. | |
| Class Assignments: Conduct a titrimetric ammonia determination | |

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|---|---|
| Module No: | Topic: Determination of Ammonia by Titrimetric Method |
| Instructor Notes: | Instructor Outline: |
| <p>Handout</p> <p>Ammonia Procedures Titrametric Sections 5 and 6 Pages 38 - 42</p> <p>Handout</p> <p>Ammonia Procedure Titrametric Pages 38 - 42</p> <p>Overhead</p> <p>Handout Ammonia Procedures Titrametric Section 8 Pages 38 - 42 Page 26</p> | <ol style="list-style-type: none"> 1. Apparatus and reagents <ol style="list-style-type: none"> a. Show and describe the apparatus needed for the titrametric method. b. List the reagents needed and indicate the availability of pre-made reagents. 2. Procedure <ol style="list-style-type: none"> a. Demonstrate the titrametric method b. Have participants perform an ammonia determination using the titrametric method. 3. Calculations <ol style="list-style-type: none"> a. Demonstrate the calculations used in the titrametric method. |

NITROGEN, AMMONIA

Distillation Titration Procedure

1. Scope and Application

1.1 This distillation method covers the determination of ammonia-nitrogen exclusive of total Kjeldahl nitrogen, in drinking, surface, and saline waters, domestic and industrial wastes. It is the method of choice where economics and sample load do not warrant the use of automated equipment.

1.2 The method covers the range from 1.0 to 25 mg/l for the titrimetric procedure.

2. Summary of Method

2.1 The sample is buffered at a pH of 9.5 with a borate buffer in order to decrease hydrolysis of cyanates and organic nitrogen compounds, and is then distilled into a solution of boric acid. The ammonia in the distillate is determined titrimetrically with standard sulfuric acid to a pH end point of 4.8.

3. Sample Handling and Preservation

3.1 Samples may be preserved with 2 ml of conc. H_2SO_4 or 40 mg $HgCl_2$ per liter and stored at 4° C.

4. Interferences

4.1 Cyanate, which may be encountered in certain industrial effluents, will hydrolyze to some extent even at the pH of 9.5 at which distillation is carried out.

4.2 Residual chlorine must also be removed by pretreatment of the sample with sodium thiosulfate before distillation:

4.3 If the sample has been preserved with a mercury salt, the mercury ion must be complexed with sodium thiosulfate (0.2 g) prior to distillation.

5. Apparatus

5.1 An all-glass distilling apparatus with an 800 - 1000 ml flask.

5.2 Erlenmeyer flasks: The distillate is collected in 500 ml glass-stoppered flasks. These flasks should be marked at the 350 and the 500 ml volumes. With such marking, it is not necessary to transfer the distillate to volumetric flasks.

5.3 pH meter and electrodes

6. Reagents

6.1 Distilled water should be free of ammonia. Such water is best prepared by passage through an ion exchange column containing a strongly acidic cation exchange resin mixed with a strongly basic anion exchange resin. Regeneration of the column should be carried out according to the manufacturer's instructions.

Note: All solutions must be made with ammonia-free water.

6.2 Ammonium chloride, stock solution: 1.0 ml = 1.0 mg NH_3 -N. Dissolve 3.819 g NH_4 in distilled water and bring to volume in a 1 liter volumetric flask.

6.3 Ammonium chloride, standard solution: 1.0 ml = 0.01 mg. Dilute 10.0 ml of stock solution (6.2) to 1 liter in a volumetric flask.

6.4 Boric acid solution (20 g/l): Dissolve 20 g H_3BO_3 in distilled water and dilute to 1 liter.

6.5 pH buffers 4.00 and 7.00

6.6 Borate buffer: Add 88 ml of 0.1 N NaOH solution to 500 ml of 0.025 M sodium tetraborate solution (5.0 g anhydrous $\text{Na}_2\text{B}_4\text{O}_7$ or 9.5 g $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ per liter) and dilute to 1 liter.

6.7 Dechlorinating reagents: A number of dechlorinating reagents may be used to remove residual chlorine prior to distillation. These include:

- a. Sodium thiosulfate (1/70 N): Dissolve 3.5 g $\text{Na}_2\text{S}_2\text{O}_3$ in distilled water and dilute to 1 liter. One ml of this solution will remove 1 mg/l of residual chlorine in 500 ml of sample.
- b. Sodium arsenite (1/70 N): Dissolve 1.0 g NaAsO_2 in distilled water and dilute to 1 liter.

7. Procedure

7.1 Preparation of equipment: Add 500 ml of distilled water to an 800 ml Kjeldahl flask. The addition of boiling chips which have been previously treated with dilute NaOH will prevent bumping. Steam out the distillation apparatus until the distillate shows no trace of ammonia with Nessler reagent.

7.2 Sample preparation: Remove the residual chlorine in the sample by adding dechlorinating agent equivalent to the chlorine residual. To 400 ml of sample add 1 N NaOH (6.9), until the pH is 9.5, checking the pH during addition with a pH meter or by use of a short range pH paper.

7.3 Distillation: Transfer the sample, the pH of which has been adjusted to 9.5 to an 800 ml Kjeldahl flask and add 25 ml of the borate buffer (6.7). Distill 300 ml at the rate of 6 - 10 ml/min. into 50 ml of 2% boric acid (6.4) contained in a 500 ml Erlenmeyer flask.

Note 5: The condenser tip or an extension of the condenser tip must extend below the level of the boric acid solution. Dilute the

7.4 Determination of ammonia in distillate: Titrate the ammonia with the 0.02 N H_2SO_4 to a pH of 4.8 listing a pH meter and electrode. Titrate a blank containing the same volume of distilled water and H_3BO_3 solution.

8. Calculations

8.1 Titrimetric

$$\text{mg/l NH}_3 - \text{N} = \frac{A - B \times 280}{5}$$

Where

A = ml 0.02 N H_2SO_4 used to titrate sample

B = ml of 0.02 N H_2SO_4 used to titrate blank

S = ml sample

LABORATORY DATA SHEET

Nitrogen, Ammonia Determination
(Sample contains 1.0 to 25.0 mg/l $\text{NH}_3\text{-N}$).

Sample No. _____ Date/Time Sampled _____ Sample Point _____

(Sulfuric acid (0.02N ml _____) (0.28) (1000)

Sample ml _____ = _____ mg/liter $\text{NH}_3\text{-N}$

Analyst _____

Date _____

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|---|---|
| Module No: | Module Title: Determination of Ammonia Nitrogen |
| Approx. Time: 1 hour | Submodule Title: Topic: Introduction to the Selective Ion Ammonia Electrode |
| Objectives: Upon the completion of this topic the participant should be able to: <ol style="list-style-type: none"> 1. List interferences to the ammonia ion electrode. 2. Explain how the known addition method of analysis works. 3. Indicate when distillation is required before analysis for ammonia with the ammonia electrode. 4. Indicate how to check the slope of the ammonia electrode. | |
| Instructional Aids: Handout Known addition Ammonia Electrode Method Overheads | |
| Instructional Approach: Illustrated lecture discussion | |
| References: Instruction Manual, Ammonia Electrode by Orion Orion Methods Book EPA Methods Manual | |
| Class Assignments: | |

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| Module No: | Topic: Introduction to the Selective ion Ammonia Electrode |
| Instructor Notes: | Instructor Outline: |
| <p>Handout.</p> <p>Ammonia Electrode Method Section 1 - 4 Pages 49 - 52</p> <p>Handout</p> <p>Known addition Pages 45 - 46</p> <p>Overheads</p> <p>✓ NH₃ Electrode Page 47</p> <p>Assembly Instructions Page 48</p> | <p>1. Interferences</p> <p>a. Describe types of interferences to the ammonia electrode.</p> <p>b. Indicate how they may be eliminated.</p> <p>2. Known Addition</p> <p>a. Describe the known addition method of analysis.</p> <p>b. Demonstrate the known addition method.</p> <p>3. Slope</p> <p>a. Demonstrate how to check the slope of an electrode.</p> |

KNOWN ADDITION

Known addition is convenient for measuring occasional samples because no calibration is needed. Since an accurate measurement requires that the concentration approximately double as a result of the addition, sample concentration must be known within a factor of three. Total concentration of ammonia can be measured in the absence of complexing agents down to 6×10^{-5} M (1 ppm NH_3 or 0.8 ppm N) or in the presence of a large excess (50 to 100 times) of complexing agent. Known addition is a convenient check on the results of direct measurement.

1. Prepare a standard solution about 10 times as concentrated as the sample concentration by diluting 1000 ppm standard.
2. Add 1 ml 10 M NaOH to 100 ml of sample and place electrode in this solution. When checking a direct measurement, leave the electrode in 100 ml of the same sample solution used for direct measurement. Use magnetic stirring throughout the known addition procedure.
3. Turn function switch to REL MV. Set the reading to 000.0.
4. Pipet 10 ml of standard into the sample. Stir thoroughly. Record the potential, E.
5. From the table find the concentration ratio, Q, that corresponds to the change in potential, E. To determine the original total sample concentration, multiply Q by the concentration of the added standard:

$$C_o = QC_s$$

Where

C_o = Total sample concentration

Q = Reading from known addition table

C_s = Concentration of added standard

6. To check a direct measurement, compare results of the two methods. If they agree within $\pm 4\%$, the measurements are probably good. If the known addition result is much larger than the direct measurement, the sample may contain complexing agents.

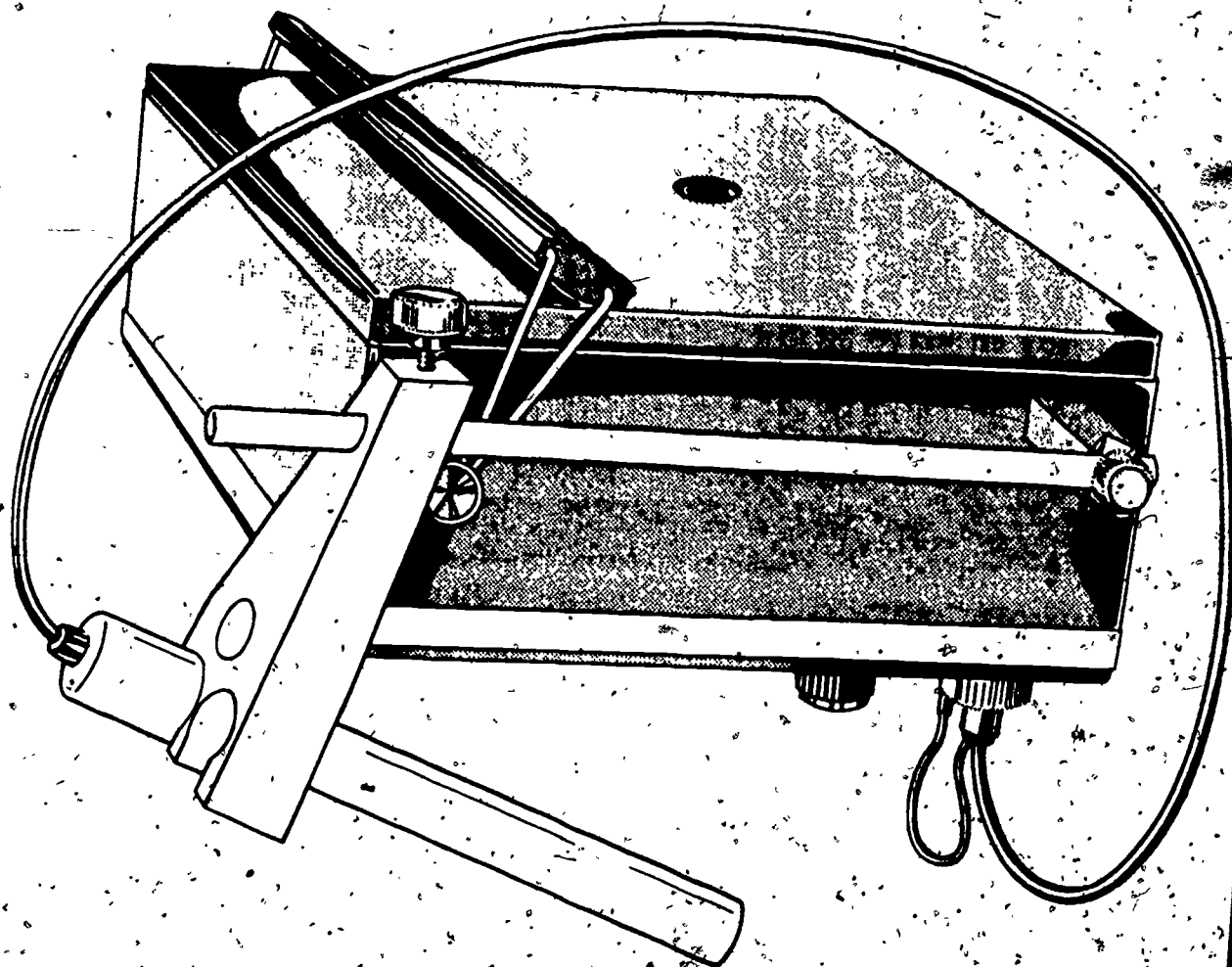
For example, suppose the addition of 10 ml 100 ppm standard solution caused a potential change of 17.8 mv. The corresponding Q value from the table is 0.0834. Total sample concentration is:

$$C_0 = QC_s$$

$$= 0.0834 \times 100$$

$$= 8.34 \text{ ppm}$$

If a previous direct measurement had given a concentration between 8.0 and 8.6 ppm, the result is probably good.



ASSEMBLY INSTRUCTIONS

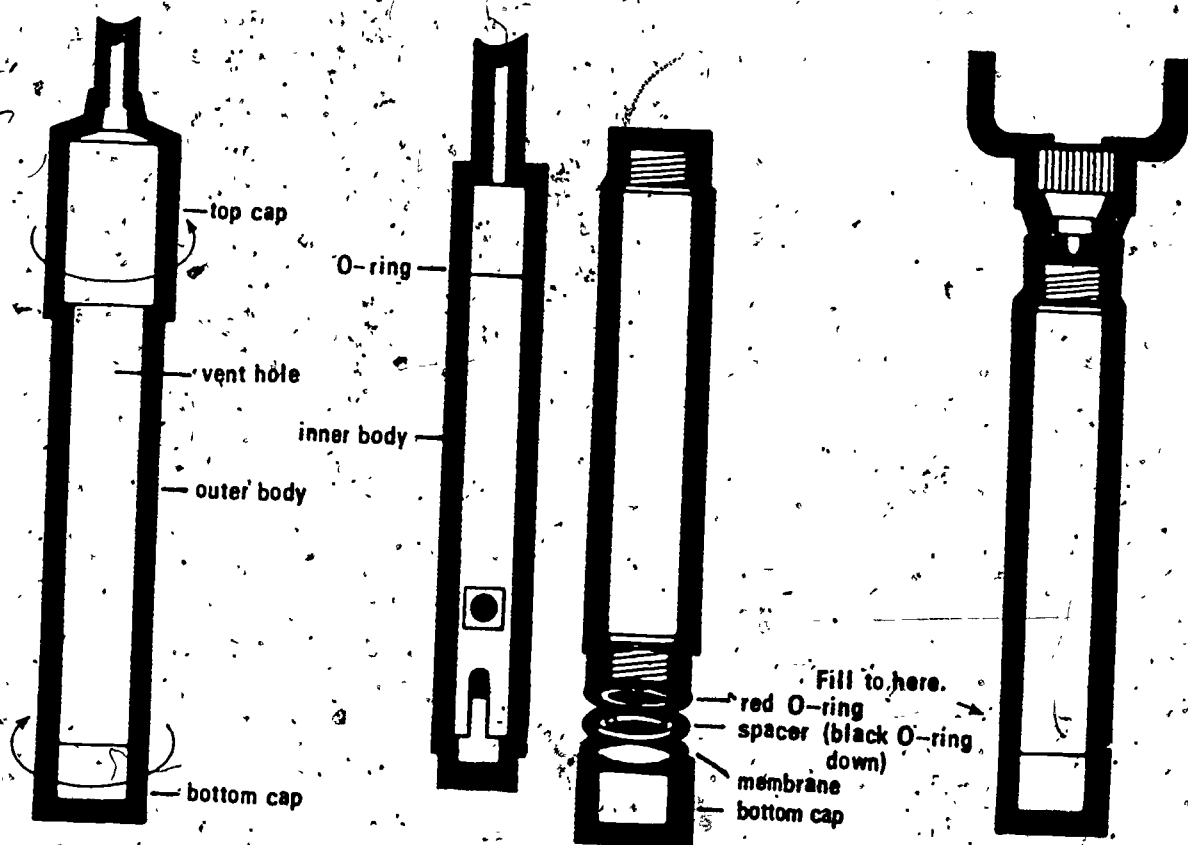


FIGURE 1

NITROGEN, AMMONIA
(Selective Ion Electrode Method)

1. Scope and Application

- 1.1 This method is applicable to the measurement of ammonia-nitrogen in drinking, surface, and saline waters, domestic and industrial wastes.
- 1.2 This method covers the range from 0.03 to 1400 mg NH_3 - N/l. Color and turbidity have no effect on the measurements and distillation is not necessary.

2. Summary of Method

- 2.1 The ammonia is determined potentiometrically using a selective ion ammonia electrode and a pH meter having an expanded millivolt scale or a specific ion meter.
- 2.2 The ammonia electrode uses a hydrophobic gas-permeable membrane to separate the sample solution from an ammonium chloride internal solution. Ammonia in the sample diffuses through the membrane and alters the pH of the internal solution, which is sensed by a -H electrode. The constant level of chloride in the internal solution is sensed by a chloride selective ion electrode which acts as the reference electrode.

3. Sample Handling and Preservation

- 3.1 Preserve by refrigeration at 4° C; analyze within 24 hours. If longer holding times are desired, preserve with 2 ml conc. H_2SO_4 (pH.2).

4. Interferences

- 4.1 Volatile amines act as a positive interference.

4.2 Mercury interferes by forming a strong complex with ammonia. Thus the samples cannot be preserved with mercuric chloride.

5. Apparatus

5.1 Electrometer (pH meter) with expanded mV scale or a specific ion meter.

5.2 Ammonia selective electrode, such as Orion Model 95 - 10 or EIL Model 8002-2.

5.3 Magnetic stirrer, thermally insulated, and Teflon-coated stirring bar.

6. Reagents

6.1 Distilled water: Special precautions must be taken to insure that the distilled water is free of ammonia. This is accomplished by passing distilled water through an ion exchange column containing a strongly acidic cation exchange resin mixed with a strongly basic anion exchange resin.

6.2 Sodium hydroxide, 10N: Dissolve 400 g of sodium hydroxide in 800 ml of distilled water. Cool and dilute to 1 liter with distilled water (6.1).

6.3 Ammonium chloride, stock solution: $1.0 \text{ ml} = 1.0 \text{ mg NH}_3 - \text{N}$. Dissolve 3.819 g $\text{NH}_4 \text{Cl}$ in water and bring to volume in a 1 liter volumetric flask using distilled water (6.1).

6.4 Ammonium chloride, standard solution: $1.0 \text{ ml} = 0.01 \text{ mg NH}_3 - \text{N}$. Dilute 10.0 ml of the stock solution (6.3) to 1 liter with distilled water (6.1) in a volumetric flask.

Note 1: When analyzing saline waters, standards must be made up in synthetic ocean water (SOW); found in Nitrogen, Ammonia; Automated Colorimetric Phenate Method.

7. Procedure

7.1 Preparation of standards: Prepare a series of standard solutions

covering the concentration range of the samples by diluting either the stock or standard solutions of ammonium chloride.

7.2 Calibration of electrometer: Place 100 ml of each standard solution in clean 150 ml beakers. Immerse electrode into standard of lowest concentration and add 1 ml of 10N sodium hydroxide solution while mixing. Keep electrode in the solution until a stable reading is obtained.

Note 2: The pH of the solution after the addition of NaOH must be above 11. Caution: Sodium hydroxide must not be added prior to electrode immersion, for ammonia may be lost from a basic solution.

7.3 Repeat this procedure with the remaining standards, going from lowest to highest concentration. Using semilogarithmic graph paper, plot the concentration of ammonia in mg $\text{NH}_3 - \text{N/l}$ on the log axis vs. the electrode potential developed in the standard on the linear axis, starting with the lowest concentration at the bottom of the scale.

7.4 Calibration of a specific ion meter: Follow the directions of the manufacturer for the operation of the instrument.

7.5 Sample measurement: Follow the procedure in (7.2) for 100 ml of sample and convert the potential reading to the ammonia concentration using the standard curve. If a specific ion meter is used, read the ammonia level directly in mg $\text{NH}_3 - \text{N/l}$.

8. Precision and Accuracy

8.1 In a single laboratory (MDQARL), using surface water samples at concentrations of 1.00, 0.77, 0.19, and 0.13 mg $\text{NH}_3 - \text{N/l}$, standard deviations were ± 0.017 , ± 0.003 , respectively.

8.2 In a single laboratory (MDQARL), using surface water samples at concentrations of 0.19 and 0.13 $\text{NH}_3 - \text{N/l}$, recoveries were 96% and 91% respectively.

BIBLIOGRAPHY

1. Booth, R. L., and Thomas, R. F., "Selective Electrode Determination of Ammonia in Water and Wastes", *Envir. Sci. Technology*, 7, p. 523 - 526 (1973).
2. Banwart, W. L., Bremner, J. M., and Tabatabai, M. A., "Determination of Ammonium in Soil Extracts and Water Samples by an Ammonia Electrode", *Comm. Soil Sci. Plant Anal.*, 3 p. 449 (1972).
3. Midgley, D., and Torrance, K., "The Determination of Ammonia in Condensed Stream and Boiler Feed-Water with a Potentiometric Ammonia Probe", *Analyst*, 97 p. 626 - 633 (1972).

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| Module No: | Module Title: Determination of Ammonia Nitrogen Submodule Title: |
| Approx. Time: 2 hours | Topic: Determination of Ammonia using Ammonia Electrode |
| Objectives: Upon the completion of this topic the participant should be able to: <ol style="list-style-type: none"> 1. Identify the proper apparatus and reagents needed for the ammonia nitrogen test by selective ion electrode. 2. Conduct an ammonia nitrogen test using the ammonia electrode to produce a calibration graph from known standards and compare the sample to the knowns using the calibration graph. 3. Conduct an ammonia nitrogen test using the ammonia electrode by known addition methods. 4. Translate the raw data from the selective ion electrode methods into appropriate methods of expression. | |
| Instructional Aids: Handouts Known addition methods Ammonia Electrode Procedure | |
| Instructional Approach: Laboratory | |
| References: EPA Methods Manual Instruction Manual, Ammonia Electrode | |
| Class Assignments: Conduct an ammonia test using the ammonia electrode | |

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| Module No: | Topic: Determination of Ammonia using Ammonia Electrode |
| Instructor Notes: | Instructor Outline: |
| Handout Ammonia Electrode Procedure Section 3 - 6 Pages 49 - 52 Handout Pages 49 - 52 Ammonia Electrode Procedure Section 7 | <ol style="list-style-type: none">1. Apparatus and reagents<ol style="list-style-type: none">a. Show and describe the apparatus needed for determination of ammonia with an electrode.b. Demonstrate the makeup of required reagents and indicate the availability of premade reagents.2. Ammonia Determination<ol style="list-style-type: none">a. Demonstrate the ammonia nitrogen test using the ammonia electrode.b. Have participants conduct an ammonia nitrogen test using the ammonia electrode.3. Calculations<ol style="list-style-type: none">a. Demonstrate the conversion of raw data into standard units.b. Have participants calculate results. |

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| Module No: | Module Title: Determination of Ammonia Nitrogen |
| Approx. Time: 1 hr | Submodule Title: Topic: Review |
| Objectives: Review of all objectives in module | |
| Instructional Aids: All handouts used in module | |
| Instructional Approach: Discussion | |
| References: All references listed in module | |
| Class Assignments: Select the best method given home, plant conditions | |

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| Module No: | Topic: Review |
| Instructor Notes: | Instructor Outline: <ol style="list-style-type: none">1. Review each of the methods.2. Have participants select the best method for their home plant considering, cost of equipment and reagents, analysis time, sensitivity of method, and interferences. |

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| Module No: | Module Title: |
| Approx. Time: | Submodule Title: |
| | EVALUATION |

Objectives:

1. The sensitivity of the titrimetric method without dilution is
 - ☐ 10 to 50 mg/l NH_3 as N
 - ☐ .5 to 25 mg/l NH_3 as N
 - ☐ .05 to 1 mg/l NH_3 as N
 - ☐ .02 to 1000 mg/l NH_3 as N
2. T F Dilution is a problem in the nesslerization method because dilution water may have ammonia in it.
3. What methods do most kits use
 - ☐ Nesslerization
 - ☐ Titrimetric
 - ☐ Electrode
4. T F The ammonia electrode method is EPA approved
5. T F The kits are EPA approved
6. T F Direct nesslerization is EPA approved
7. T F An ammonia sample may be preserved with acid and cooling for 24 hours.
8. Indicate the methods for ammonia nitrogen
 - ☐ Nesslerization method
 - ☐ Total Kjeldahl nitrogen method
 - ☐ Potentiometric with electrode method
 - ☐ Titrimetric method
 - ☐ Gravimetric method
 - ☐ Cadmium reduction method

9. The chemical symbol for ammonia is:

☐ NH_4^+

☐ NH_3

☐ NH_2

☐ NO_3

10. Standard Methods reports ammonia results as

☐ mg/l NH_4^+

☐ mg/l NH_3

☐ mg/l NH_3 as N

11. T F The ammonia titration procedure must be preceded by the distillation step.
12. T F All of the ammonia procedures have some interferences.
13. T F Soaps and other wetting agents may interfere with the ammonia electrode operator.

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|-------------------|--|
| Module No: | Topic: EVALUATION |
| Instructor Notes: | Instructor Outline: |
| | <ol style="list-style-type: none">1. .5 to 25 mg/l NH_3 as N2. True3. Nesslerization4. True5. False6. False7. True8. Nesslerization Potentiometric with electrode Titrimetric9. NH_310. mg/l NH_3 or N11. True12. True13. True |